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Synthesis and spectra of novel diorganotellurides and diorganoditellurides. Potential polydentate hybrid organotellurium ligands

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Abstract

Nine new potential polydentate hybrid organotellurium ligands, namely bis(2-aminoethyl)telluride and ditelluride (**1**,**3**), bis(2-dimethylaminoethyl)telluride and ditelluride (**2**,**4**), 2-(dimethylamino)ethyl aryl telluride (**5**), 2-methoxyethyl aryl telluride (**6**), bis(2-aryltelluroethyl)ether (**7**), 1,2-bis(2-aryltelluroethoxy)ethane (**8**) and *N*,*N*,*N*′,*N*′-tetrakis(2-aryltelluroethyl)ethane-1,2-diamine (**9**), (where aryl = 4-MeO-C_6H_4), have been made in 60–85% yield by the reaction of Na_2Te/Na_2Te_2 or $ArTe^-Na^+$ with the appropriate organic halide. Compounds **6–8** cannot be stored for more than a week and undergo aerial oxidation to give R_2TeO species. All the compounds **1–9** have been characterized by molecular weight determination, elemental analyses and ^1H NMR and $^{13}C\{^1H\}$ spectroscopy.

Keywords: Tellurium; Polydentate ligands; Diorganotellurides; Diorganoditellurides

1. Introduction

There is much interest in the chemistry of polydentate tellurium-containing ligands, including hybrid species and thus five reviews [1–5] on the subject have appeared in the last decade. The main reasons for this interest lie in the possible applications of the species in chemical vapour deposition processes [6] for the thin film fabrication of new electronic materials such as II–IV semiconductors and in the fact that tellurium has an isotope of half integral spin with reasonable natural abundance suitable for NMR investigations [5,7]. Thus, a metal–tellurium bond in solution can be more readily studied than the corresponding metal–sulphur bond. We have recently made several novel multidentate hybrid organotellurium ligands [4,8–10] and in continuation of these studies we thought it worthwhile to synthesize the diorgano tellurides and ditellurides **1–9** which could be used as hybrid organotellurium ligands. The synthesis and spectra of these tellurides and ditellurides are the subject of the present paper. To the best of our knowledge the syntheses of compounds **1–9** have not been reported previously.

2. Experimental details

Published methods were used to synthesize bis(4-methoxyphenyl)ditelluride [11], disodium telluride [12], disodium ditelluride [12] and *N*,*N*,*N*′,*N*′-tetrakis[2-chloroethyl]ethane-1,2-diamine [13]. 2-Bromoethylamine monohydrobromide, 2-dimethylamino ethylchloride monohydrochloride, 2-chloroethyl methyl ether, bis(2-chloroethyl)ether and 1,2-bis(2-chloroethoxy)ethane were used as received from Aldrich or Fluka. Elemental analysis and physical measurements were carried out as described previously [14].

2.1. Synthesis of 1–4

The colourless suspension of Na_2Te (10 mmol) or deep purple solution of Na_2Te_2 (10 mmol) made by the

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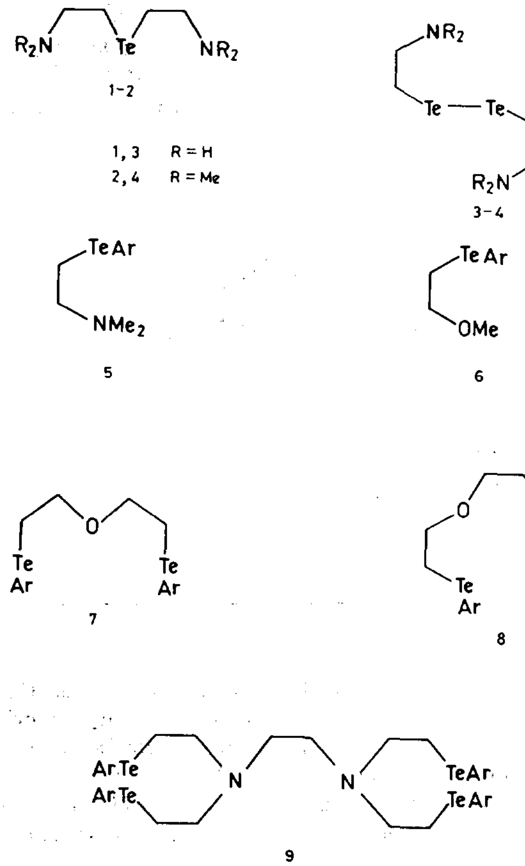


Formule 1.

published method [12] was mixed under nitrogen with a solution of $BrCH_2CH_2NH_2$ or $ClCH_2CH_2NMe_2$ (20 mmol) in 5 cm^3 of ethanol and the mixture was refluxed for 0.5 h. It was then cooled to 25°C and added to 100 cm^3 of water. The product was extracted into diethyl ether isolated as viscous liquids by evaporating off the diethyl ether.

2.2. Synthesis of 5–8

A colourless solution of 4 mmol of $[4\text{-}MeOC_6H_4Te]^-[Na]^+$ generated in situ in 35 cm^3 of 85/15 EtOH-H_2O by the published method [8,9,14] was mixed with a solution of the relevant organic halide (4 mmol for **5** and **6** but 2 mmol for **7** and **8** in 5 cm^3 of ethanol). The mixture was refluxed for 2–3 h then cooled to 25°C and added to 200 cm^3 of water. The products were extracted into diethylether and isolated as viscous liquids by evaporation of the ether.

2.3. Synthesis of 9

A solution of *N,N,N′,N′*-tetrakis[2-chloroethyl] ethane-1,2-diamine dihydrochloride [13] (1 mmol) in ethanol was added under nitrogen to $[4\text{-}MeOC_6H_4Te^-Na^+]$ (4 mmol) dropwise with refluxing under nitrogen atmosphere. After complete addition the reaction mixture was refluxed further for 2 h and cooled to 25°C. The **9** was extracted from the reaction mixture into CH_2Cl_2 and obtained as off-white solid by evaporating off the solvent.

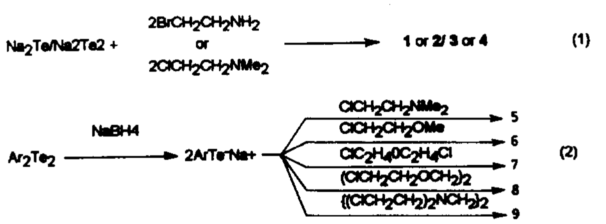
3. Results and discussion

Compounds **1–9** were obtained from the reactions shown in Eqs. (1) and (2). The yields were good (60–

Table 1
Physical properties and elemental analyses of tellurides and ditellurides (**1–9**)

Telluride/ Ditelluride	Colour and physical state	Yield (%)	Analyses: Found (calc.)%				Mol wt Found (Calc.)
			C	H	N	Te	
1	Orange yellow liquid	65	22.03 (22.26)	5.27 (5.56)	13.13 (12.98)	58.50 (59.18)	200.0 (215.6)
2	Yellow liquid	70	35.08 (35.39)	7.01 (7.36)	10.52 (10.30)	46.00 (46.98)	265.0 (271.6)
3	Red liquid	60	14.28 (13.98)	3.62 (3.90)	8.39 (8.15)	73.50 (74.35)	340.0 (343.2)
4	Red liquid	60	23.69 (24.04)	4.89 (5.01)	7.23 (7.01)	62.80 (63.92)	390.0 (399.2)
5	Pale yellow liquid	80	43.28 (43.05)	5.28 (5.59)	4.78 (4.56)	41.00 (41.62)	300.0 (306.6)
6	Pale yellow liquid	85	40.96 (40.87)	4.93 (4.26)	– –	42.90 (43.46)	291.0 (293.6)
7	Pale yellow liquid	75	40.53 (39.91)	4.52 (4.06)	– –	46.80 (47.15)	535.0 (541.2)
8	Pale yellow liqud	70	40.88 (41.01)	4.78 (4.49)	– –	43.00 (43.60)	580.5 (585.2)
9	Off white solid (m.p. 100–102°C) [a]	68	40.57 (41.21)	4.07 (4.33)	2.79 (2.52)	45.80 (46.13)	1085.0 (1106.4)

[a] Determined in capillary tube



Formule 2.

85%). However, compounds **6–8** begin to decompose after storage for 4–5 days and undergo aerial oxidation to give the compounds R_2TeO, which can be reduced with hydrazine to regenerate **6–8**. On storage for a month in air, however, elemental tellurium separates out. The syntheses of ditellurides **3** and **4** are of significance because very few functionalized ditellurides [1–4] capable of forming chelates have been reported previously. Moreover, these ditellurides can be readily reduced by $NaBH_4$ to give the corresponding hybrid organotellurium anions $[R_2NCH_2CH_2Te]^-$ (the use of a functionalized organotellurolate as a ligand has not so far been investigated [1–3]). All the organotellurides and diorganoditellurides (**1–9**) were characterized by elemental analysis, molecular weight determination and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Data with assignments are shown in Tables 1–3. The assignments of $^{13}C\{^1H\}$ NMR spectra are based on previous analyses [15]. In the $^{13}C\{^1H\}$ NMR spectrum of **6** the OMe signal appearing at the low field appears to come from the OMe attached to the aromatic ring since the alkyl group would have the larger +I effect. The ^1H NMR spectrum of **7** exhibits well resolved signals for OCH_2 and $TeCH_2$ in contrast to its nitrogen analogue [14], $HN(CH_2CH_2TeAr)_2$, this is attributable to the higher electronegativity of oxygen than of nitrogen. There is similar resolution in the ^1H NMR spectrum of $CH_3N(CH_2CH_2TeAr)_2$. Owing to the weaker coordinating ability of ether centres relative to alkyl amine centres it is likely that **7** will coordinate through two tellurium atoms only to form a large size chelate ring suitable for connecting two trans sites of a square

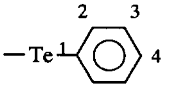
Table 2
^1H NMR data for **1–9**

Telluride/ ditelluride	Chemical shift (δ, ppm), $CDCl_3$					
	$-CH_2$-N-/ $-CH_2$-O	$-CH_2$-Te	NMe_2/ $-NH_2$/OMe	OMe of Ar	ArH *o* to Te	ArH *m* to Te
1	2.90–3.10(t, 4H)	2.65–2.80(t, 4H)	1.65(s, 4H)	–	–	–
2	← 2.29–3.06(m, 8H) →		2.23(s, 12H)	–	–	–
3	← 2.62–3.41(m, 8H) →		1.44(s, 4H)	–	–	–
4	2.96–3.04(t, 4H)	2.68–2.72(t, 4H)	2.24(s, 12H)	–	–	
5	← 2.59–3.08(m, 4H) →		2.23(s, 6H)	3.79(s, 3H)	6.79–6.98(d, 2H)	7.79–7.87(d, 2H)
6	3.60–3.75(t, 2H)	2.89–3.04(t, 2H)	← 3.33(s, 6H) →		6.70–6.80(d, 2H)	7.60–7.73(d, 4H)
7	3.64–3.82(m, 10 H)	2.86–3.00(t, 4H)	–	merged with OCH_2	6.69–6.70(d, 4H)	7.60–7.71(d, 4H)
8	3.53–3.82(m, 14H)	2.87–3.02(t, 4H)	–	merged with OCH_2	6.68–6.76(d, 4H)	7.62–7.71(d, 4H)
9	2.76–3.03(m, 12H)	2.48(bs, 8H)	–	3.79(s, 12H)	6.70–6.78(d, 8H)	7.25–7.70(d, 8H)

bs broad singlet

Table 3
$^{13}C\{^1H\}$ NMR data for **1–9**

Telluride/ ditelluride — Chemical shift (δ, ppm), $CDCl_3$



Telluride/ ditelluride	NMe_2	OMe [a]	OMe [b]	OCH_2	$TeCH_2$	$-NCH_2-$	$-NC_2H_4-N-$ $-OC_2H_4-O-$	C_1	C_2	C_3	C_4
1	–	–	–	–	8.2	43.4	–	–	–	–	–
2	44.3	–	–	–	0.3	60.6	–	–	–	–	–
3	–	–	–	–	10.4	44.4	–	–	–	–	–
4	44.3	–	–	–	4.8	60.8	–	–	–	–	–
5	44.5	–	54.6	–	8.1	60.0	–	100.7	140.1	114.5	159.0
6	–	54.8	57.8	73.4	7.9	–	–	99.8	140.1	114.8	159.5
7	–	–	54.7	71.2	8.1	–	–	99.7	140.4	114.7	159.3
8	–	–	54.6	69.4	8.0	–	72.0	99.8	140.3	114.7	159.3
9	–	–	52.4	–	8.2	58.6	55.0	101.3	140.4	114.9	159.3

[a] Linked to CH_2CH_2Te [b] Linked to phenyl ring

complex of palladium(II) or platinum(II). A similar possibility exists for **8**. The nitrogen analogue of **7** acts as a tridentate ligand in square planar platinum(II) complexes [10] and therefore appears to be unsuitable for the formation of large rings. Compound **9** appears to be the first example of a potentially hexadentate tellurium ligand. The phosphorus and arsenic analogues of **9** are known to form interesting copper(I) complexes [13]. There are also only very few examples of tetradentate tellurium ligands [4] and thus the synthesis of **8** in good yield is of significance in this context.

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